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An Electron Microscopic Study on the Suspenoid for the Nephelometry of Sulfate Ion*

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The electron microscopic observation of suspended particles of barium sulphate revealed that the nephelometric method of the estimation of sulphate ion in water as barium sulphate gives different shape and size by the least change of concentration of sulphate ion. The authors obtained dendritic suspended particles of $0.6 \times 0.15 \mu$ in size by the formation of the suspension in 50% alcohol and the suspended particles are uniform in shape and size within the limit of concentration of sulphate ion present in natural water. By the use of this method the error of estimation is minimized within several per cent. The data of estimation by this nephelometry and by the gravimetric method were discussed.

I. INTRODUCTION

The authors have made a systematic study on barium sulphate precipitates produced in various total concentrations in the media of water and of alcohol solution by means of the electron microscopy^{1,2)}. The size and shape of barium sulphate precipitates were varied by changing the total concentration and the solubility of barium sulphate.

Generally, at the nephelometry the suspenoid is necessary not to settled down and the size and shape of the particles of the suspenoid is obliged to keep constant in the range of the concentration to be applied the nephelometry. To make proportionate the concentration of sulphate in the sample to the concentration of the suspension many investigations have been made regarding the formation of the suspension, but very few with respect to the shape and size of the suspenoid. As the authors have found that the size and shape of the barium sulphate precipitates were largely changed with a small difference of the total concentration, the size and shape of the suspenoid at the nephelometry were observed by an electron microscope and the condition of the nephelometry was examined.

II. EXPERIMENT

(1) Nephelometer

The Duboscq colourimeter was used as a nephelometer with a little improve-

* This is a translation of the same article which appeared in Japanese in *Japan Analyst*, **3**, 291~3 (1954).

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ment. The front door of the Duboscq colourimeter was taken off and the two new doors were set at the upper and the lower parts. The parallel ray which passed the green filter was made to fall on the cups kept out of the light from the bottom.

(2) Use of the nephelometer

The ray was thrown at right angle upon the both cups filled with a standard and a sample suspensions. The cup containing a standard suspension was set at exactly 20.00 or 30.00 (scale of nephelometer extended from 0 to 50 divisions) and the other cup containing a sample suspension was raised or lowered until equal intensity of the scattered light was obtained in the two fields. The concentration of the sample was determined from the reading and the calibration curve obtained beforehand.

(3) Electron microscopic observation on the shape and size of the suspenoid

One drop of the suspension was mounted on the specimen holder for the electron microscopy and dried. The specimen was observed by the electron microscope SM-T4.

III. USUAL WATER SUSPENSION METHOD

In general, the nephelometry of sulphate in water is usually practiced as follows: To a definite amount of the sample water are added a little hydrochloric acid, gelatin solution and barium chloride solution, then is added the distilled water to make up to a definite volume. This suspension is compared with the standard suspension prepared in a similar way. To criticise this usual method, the fundamental experiments were conducted as follows.

(1) To 0.5 ml. of 0.020 N sulphuric acid were added 1 ml. of 0.1 N hydrochloric acid, 2 ml. of 0.05 % gelatin solution and 2 ml. of 0.1 N barium chloride solution, then was added water to make up to 50 ml.

In this case the precipitate began to deposit about 2 minute after the addition of barium chloride solution and the turbidity became maximum after several minutes. The suspension had silk-like lustre. The particles of the suspenoid were thin rectangular crystals and the size was $3.2 \times 2.5 \times 0.2 \mu$ on average as shown in Fig. 2.

(2) 1.0 ml. of 0.020 N sulphuric acid was treated in a similar way as described in (1).

The precipitate deposited similar to (1) and the particles were thin rectangular. But the size was $1.6 \times 0.9 \times 0.1 \mu$, that is, the length of a side was one second of that of the former suspended particles as shown in Fig. 3.

The size of the suspended particles of barium sulphate prepared in water was varied by a little change of the concentration of sulphate and the suspenoid settled down 1 hour after mixing the reagents.

By changing the concentration of sulphuric acid the suspensions were prepared and the calibration curve for the nephelometry was obtained. This calibration curve is indicated as 1 in Fig. 1. The error of the calibration curve is within $\pm 15\%$.

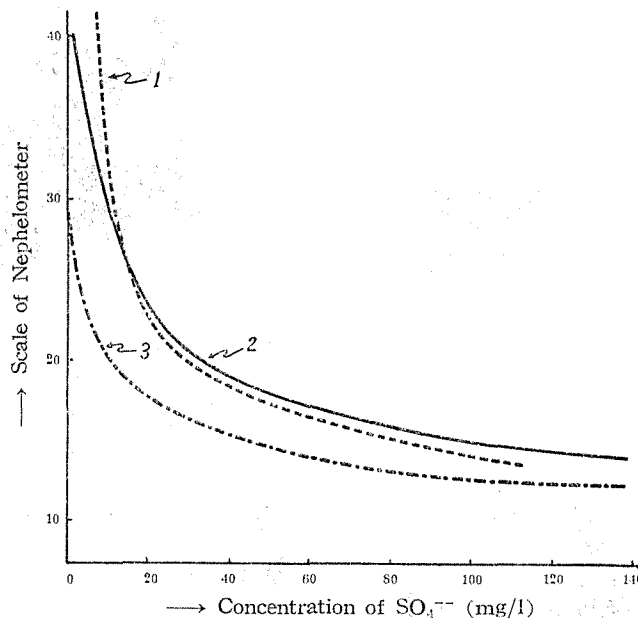


Fig. 1. Calibration Curves

IV. ALCOHOL SOLUTION METHOD

The suspenoid of barium sulphate having the constant size and shape at various concentrations of sulphate were obtained by addition of alcohol. As reported previously, the size of the barium sulphate precipitate formed in 50% alcohol solution is almost constant at various total concentrations². From this standpoint the preparation of the suspension in 50% alcohol solution was studied.

(3) To 1.0 ml. of 0.020 N sulphuric acid were added 1 ml. of 0.1 N hydrochloric acid, 25 ml. of alcohol, 2 ml. of 0.05 % gelatin solution and 2 ml. of 0.1 N barium chloride solution, then was added water to make up to 50 ml.

In this case the suspension was formed directly after mixing the reagents. The suspended particles were thin and dendritic as shown in Fig. 4. The length was 0.6μ and the width was 0.15μ . The suspension prepared by this method was stable for about 1 month.

(4) 0.3 ml. of 0.020 N sulphuric acid was treated in a similar way as described in (3).

The suspended particles were the same in size and shape with those of (3) as shown in Fig. 5.

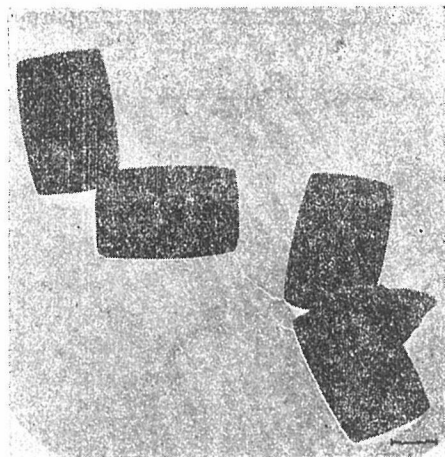


Fig. 2. ($\times 6,000$)

0.020 N H_2SO_4	0.5ml.	
0.1 N HCl	1.0ml.	
0.05 % gelatin solution	2.0ml.	→50ml. suspension
0.1 N BaCl_2	2.0ml.	

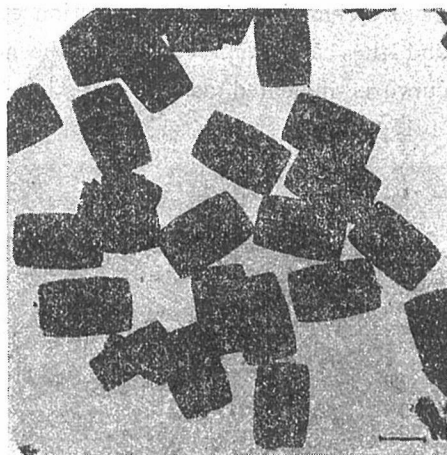


Fig. 3. ($\times 6,000$)

0.020 N H_2SO_4	1.0ml.	
0.1 N HCl	1.0ml.	
0.05 % gelatin solution	2.0ml.	→50ml. suspension
0.1 N BaCl_2	2.0ml.	



Fig. 4. ($\times 10,000$)

0.020 N H_2SO_4	1.0ml.	→50ml. suspension
0.1 N HCl	1.0ml.	
alcohol	25.0ml.	
0.05 % gelatin solution	2.0ml.	
0.1 N BaCl_2	2.0ml.	

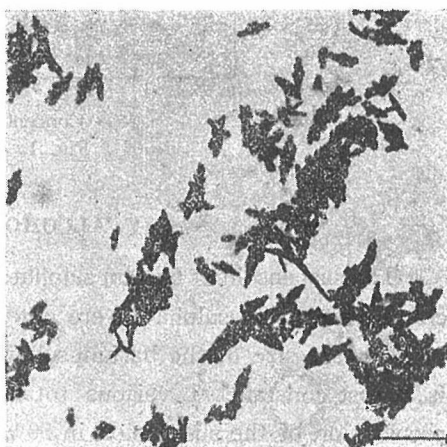


Fig. 5. ($\times 10,000$)

0.020 N H_2SO_4	0.3ml.	→50ml. suspension
0.1 N HCl	1.0ml.	
alcohol	25.0ml.	
0.05 % gelatin solution	2.0ml.	
0.1 N BaCl_2	2.0ml.	

By changing the concentration of the sulphuric acid the suspension was prepared in the similar way and the calibration curves were obtained. The suspensions described in (5) and (6) were used as the standard.

(5) 0.5 ml. of 0.020 N sulphuric acid was treated in the similar way as described in (3).

(6) Sulphuric acid was not used but the other reagents were mixed in the similar way.

When the suspension of (5) is used as the standard, the cup containing it was set at 20.00 of the reading and the other cup was balanced against it. When the solution of (6) was used as the standard, the cup containing it was set at 30.00. The calibration curves are indicated at 2 and 3 in Fig. 1 for the standard of (5) and (6) respectively. For convenience of the measurement of sulphate contained in the sample water, the concentration of sulphate in Fig. 1 is graduated so that the number of mg of sulphate per liter of the sample water can be known directly from the reading the scale of the nephelometer.

The effects of the other ions. The ions or salts less than the concentration described below does not affect the alcohol solution method. That is, the size and shape of the particles of the suspensoid were not affected by the electrolytes less than the following concentrations.

NaCl	0.03 M	KCl	0.004 M	NH ₄ Cl	0.12 M
MgCl ₂	0.002 M	CaCl ₂	0.002 M	NaHCO ₃	0.003 M
NaHPO ₄	0.002 M				

Measurable range and error. Measurable range of this method for the determination of sulphate in 4 to 80 mg of sulphate per liter. For the sample containing sulphate 4 to 20 mg per liter the calibration curve 2 is used and 20 to 80 mg per liter the curve 3 is used. The error of the calibration curves is as follows:

Curve 2 (4~20 mg SO₄⁻⁻/l) : $\pm 8 \%$

Curve 3 (20~80 mg SO₄⁻⁻/l) : $\pm 4 \%$

V. APPLICATION

The examples of the usual method and the new alcohol solution method to determine the concentration of sulphate in water are described below.

(1) The usual water suspension method

To 15 ml. of sample solution were added 1 ml. of 0.1 N hydrochloric acid, 2ml. of 0.05 % gelatin solution and 2 ml. of 0.1 N barium chloride solution, then was added water to make up to 50 ml. The prepared suspension was compared with the standard suspension as described in (1) in the above section. Some of the results are shown in Table 1.

(2) The new alcohol solution method

To 15 ml. of the sample water were added 1 ml. of 0.1 N hydrochloric acid, 25 ml. of alcohol, 2 ml. of 0.05 % gelatin solution and 2 ml. of 0.1 N barium chloride solution, then was added water to make up to 50 ml. The prepared suspension was compared with the standard suspension of (5) or (6) in the above section. The results of measurements of sulphate in some kinds of water are shown in Table 1.

As shown in Table 1, the error of the measurements by the usual method is

Table 1. The concentration of sulphate in water.

Sample (Date)	Gravimetric analysis mg/l	Usual water suspension method		Alcohol solution method	
		mg/l	error* mg/l	mg/l	error* mg/l
Well-water of the Institute of the authors (1952.8.29)	44.0	48.0	+ 4.0	44.0	0.0
" (1952.10.2)	29.2	—	—	29.0	— 0.2
City-water of Kyoto (1952.10.6)	—	—	—	12.0	—
" (1953.2.5)	15.0	12.0	— 3.0	16.0	+ 1.0
City-water of Takatsuki (1952.10.6)	17.0	21.0	+ 3.5	19.0	+ 1.5
Akuta-river in Takatsuki (1952.10.6)	21.1	35.0	+13.9	22.0	+ 0.9
Rain-water at Takatsuki (1952.10.8)	8.0	—	—	9.0	+ 1.0

* The error is the difference with the gravimetric analysis.

great for the gravimetric analysis. The error is probably based upon the irregularity of the size and shape of the suspended particles. But the error is greatly reduced by the authors' alcohol solution method and the results are almost satisfactory.

Further, if the electrophotonephelometer is used as the nephelometric instrument like Toennies,³⁾ the results must be more exact.

VI. SUMMARY

(1) By the electron microscopic observation it was demonstrated that the size and shape of the suspensoid have to be constant in the case of the nephelometry.

(2) When the suspension of barium sulphate is prepared in 50 % alcohol solution, the size and shape of the suspensoid become definite, and the error in the case of nephelometry of sulphate is within several per cents. The suspension is very stable and the standard suspension can be used for several weeks.

(3) To determine sulphate in water by means of the usual water suspension method, the calibration curve must be obtained very carefully.

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